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Spiliotopoulou, Aikaterini; Hansen, Kamilla Marie Speht; Andersen, Henrik Rasmus

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Photolysis and secondary formation of disinfection by-products by UV treatment of swimming pool water

A. Spiliotopoulou, DTU, K.M.S. Hansen, DTU*, H.R. Andersen, DTU**

Abstract: Swimming is popular to people as it is beneficial to fitness and health. Bathers release pathogens, organic and nitrogenous compounds in to water. Thus, disinfection and cleaning treatments are necessary. Chlorinated disinfection by-products (DBPs) in swimming pools are a known health concern. UV treatment efficiently removes chloramines but has been reported to produce other DBPs, but the mechanism is unknown. The goal of this work was to investigate the effects of medium-pressure ultraviolet (UV) lamp radiation on the water quality of chlorinated indoor swimming pools in the presence of different species that reacts with UV: chlorine (Cl_2), hydrogen peroxide (H_2O_2) and nitrate (NO_3^-) describing the mechanisms that DBP formation is based on. Post UV chlorine consumption was found to vary significantly among treatments and swimming pools depending on their matrix characteristics. Post UV chlorination amplified DBP formation. Results suggest that chloroforms are not formed in the photo-reactor but afterwards, when chlorine is added. Furthermore, it was found that UV released bromide and therefore the formation of brominated Trihalomethanes (THMs) increased.

It is suggested that DBPs are formed in the UV reactor. When free Cl_2 is photolyzed, •Cl and •OH are formed. Chlorine radicals react with organic matter forming DBPs. Another hypothesis suggests that UV changes the organic matter making it more reactive to Cl_2, so DBPs are formed when Cl_2 is added. Apart from hypothesises, a question has appeared. Does UV create more DBPs or just speed up their formation? The objectives of this study are to determine the effects of UV radiation on swimming pool water in presence of three radical initiators.

Treatment with UV for 20 or 40 min (UV20, UV40) did not produce THMs (Figure 1a). It was found that the main compound that is formed in Total THM (TTHM) in all water types is chloroform. Chloroform is not created during the UV exposure but after the chlorine addition (UV20 vs. UV/Cl_2, Cl_2). It could be concluded that UV/Cl_2, Cl_2, UV40/Cl_2, Cl_2 and UV, Cl_2 increase the bromine in TTHM and thus the bromide concentration in the water must have increased by the UV treatment. The reason is that UV breaks down the bonds between the carbon-based compound and bromine (Figure 2). So bromide is liberated into the water. The UV treatment also contributes to carbon activation, making it more reactive to chlorine. Then chlorine was added, post-UV, bromide is oxidiz ed to hypobromous acid, which reacts with the newly formed THM precursors and forms more bromine containing THMs that reacts further with chlorine to form Br-Cl-DBPs. Thus, bromine is transferred from the larger brominated molecules to smaller volatile compounds like BDCM and DDCM.

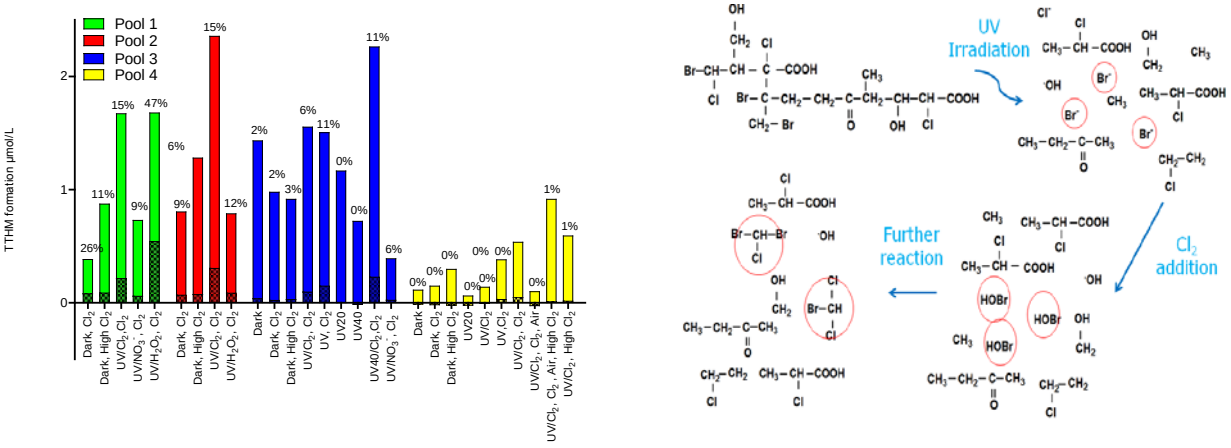

Figure 1: a) Total trihalomethane formation in water samples treated by different procedures,b) Schematic representation of brominated THM formation by chlorination post UV radiation.

To sum up, DBPs are not formed in the UV reactor but only when Cl_2 is added after the UV treatment. Thus, the first hypothesis is disapproved while results enhance the hypothesis which suggests that UV changes the carbon making it more reactive to Cl_2. Also, UV speeds up DBP formation but it is uncertain whether it increases DBP concentration or not.

* katspil@windowslive.com: Miljøvej, B113, DK-2800 Kgs. Lyngby, Denmark
* kmsh@env.dtu.dk: Miljøvej, B113, DK-2800 Kgs. Lyngby, Denmark
* hran@env.dtu.dk: Miljøvej, B113, DK-2800 Kgs. Lyngby, Denmark